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STRUCTURAL PROPERTIES OF AMORPHOUS
SEMICONDUCTORS BY MOSSBAUER SPECT-
ROSCOPY

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A. SUMMARY

The amorphous to crystalline transition in vacuum deposited tellurium films has been observed using Mossbauer spectroscopy. Although the work is still preliminary, a large difference between the amorphous and crystalline forms of tellurium has been observed in the recoil free fraction as well as a smaller, but measurable, difference between the magnitudes of the quadrupole interactions. The samples studied contain 50% enriched tellurium-125 and are about 2 microns thick. Attempts to form thicker films have met with difficulties which may be overcome in further experiments. Thicker or higher enrichment films will result in better quality spectra which will be easier to analyze and interpret.

A weak (2mCi) source of ^{125m}Te in $\beta\text{-TeO}_3$ was prepared successfully and several excellent spectra obtained. The $\beta\text{-TeO}_3$ source exhibits a recoil free fraction $f \approx 0.5$ at 80°K , which is about 3 times the f of our standard ^{125}I in Cu source. The line widths of the two sources are about equal. Unfortunately, the $\beta\text{-TeO}_3$ source is too weak to be of much use in the tellurium film experiments. We are pursuing the source problem in two ways: (a) trying to obtain a higher yield of ^{125m}Te in order to fabricate a 10mCi $\beta\text{-TeO}_3$ source, and (b) looking into the possibility of using either a ^{125}Sb in Cu or a $^{125}\text{Sb}_2\text{O}_3$ source; both sources have been reported to give

high recoil free fractions and reliable narrow emission lines. While the experiments can be done using ^{125}I in Cu as the source, the high probability of obtaining much better data by using a different source should not be overlooked.

B. MOSSBAUER EFFECT IN TELLURIUM

Details of the Mossbauer effect in tellurium and its application to the investigation of order-disorder transformations were presented in the last Semi-Annual Technical Report ⁽¹⁾ and will not be repeated here.

Recently published work ⁽²⁾ correlates the tellurium quadrupole splitting with the inverse cube of the covalent bond lengths which Te forms with its two nearest neighbors both in metallic (crystalline) Te as well as in dilute alloys of Te in the isoelectronic (crystalline) hosts Se and S. These results provide a calibration of covalent bond lengths in terms of the quadrupole splitting which should be useful for interpreting the amorphous Te structure as well as the structure of tellurium based alloys such as GeTe ⁽³⁾.

C. TECHNICAL PROGRESS

a) Spectrometer Calibration and Spectrum Analysis

As mentioned in the last Technical Report, all equipment, including the superconducting magnet system, was calibrated and modified for performing the tellurium experiments.

A new and convenient polyurethane foam dewar together with the necessary vacuum fittings and hardware were fabricated in order to simplify the routine experiments performed with both source and absorber at liquid nitrogen temperature. The variable temperature and liquid helium cryogen experiments will still have to be performed in the large double jacketed stainless steel dewar.

Spectrometer calibration has been improved using an iron foil supplied by the National Bureau of Standards as the basic transfer velocity calibration standard. Although the earlier calibrations were more than adequate for the present work, the new calibration (which is consistent with the old) shows that the velocity scale is slightly non-linear. This non-linearity in the velocity scale will be incorporated into the data analysis.

A recent communication ⁽⁴⁾ indicates that ZnTe as commercially supplied is probably not all of the cubic form, but also contains some hexagonal phase material. Using absorber samples of ZnTe prepared from single crystal chips of cubic ZnTe ⁽⁵⁾ we have found that the full width at half maximum of the Mossbauer resonance corrected for finite absorber thickness is $5.71 \pm .04$ mm/sec. The magnitude of the absorption for a 1.5 mg/cm^2 ^{125}Te absorber is 4% at 80°K using a ^{125}I in Cu source, also at about 80°K . These results indicate that our source has been among the very best

^{125}I in Cu sources ever manufactured. It is unlikely that we shall continue to be so fortunate, as ^{125}I in Cu sources are known to be highly unreproducible in terms of source line width and recoil free fraction. The present source has gone through more than three half-lives (about 200 days total) and is now only 10% as strong as it was when new. A new source of 50mCi ^{125}I in Cu has been ordered and will be checked for line width and recoil free fraction prior to examining newly prepared tellurium films.

b) Source Preparation

The technique for preparing a source in the form of $\beta\text{-TeO}_3$ containing 58 day $^{125\text{m}}\text{Te}$ was perfected in collaboration with radiochemists at New England Nuclear Corporation. A source of 2mCi $^{125\text{m}}\text{Te}$ in $\beta\text{-TeO}_3$ was prepared and used as a Mossbauer source. The results are very encouraging, especially insofar as the observed recoil free fraction at 80°K is approximately 3 times that of ^{125}I in Cu at the same temperature (0.16 versus 0.50). The line widths appear to be the same within experimental error, although the definitive test of running the new source against the new narrow line cubic ZnTe absorber was not performed because the $\beta\text{-TeO}_3$ source had decayed to an impractically weak level by the time the new ZnTe absorber became available. The difficulty with $^{125\text{m}}\text{Te}$ in $\beta\text{-TeO}_3$ sources is that until now a very low yield of $^{125\text{m}}\text{Te}$ from the ^{125}Sb parent material has been available. The method of preparation (milking $^{125\text{m}}\text{Te}$ from ^{125}Sb in an ion exchange column)

has required the use of extremely active radioactive columns to obtain a low yield of ^{125m}Te . The preparation method of neutron irradiation of ^{125}Te is being attempted in order to see whether a sufficient ($\sim 10\text{mCi}$) amount of ^{125m}Te can economically be obtained.

Another approach is to use ^{125}Sb as the gamma source. ^{125}Sb has a 2.7 year half-life versus 58 days and 60 days for ^{125m}Te and ^{125}I , respectively. It has been reported (4,6) that sources of ^{125}Sb in Cu and in Sb_2O_5 give large recoil free fractions, narrow line widths and the advantage of long half life. The principal disadvantage is that the decay scheme is not simple (7) and a 10mCi yield of 35.5 KeV gammas requires an uncomfortably high level of total radioactivity. Sources incorporating ^{125}Sb are being considered for future use.

c) Specimen Preparation

Tellurium films enriched to 50% ^{125}Te were prepared by vacuum deposition at approximately 10^{-5} Torr onto a cooled copper foil substrate. The source consisted of tellurium powder enriched to 50% ^{125}Te in a shallow vitreous carbon crucible. A fine tungsten screen covered the source material to prevent splattering. Considerable difficulty was encountered in keeping the substrate cool during the deposition. Visual observation of the film during deposition gave a good indication of the film quality. Too high a deposition rate or too much heat radiated from the evaporation furnace frequently caused

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localized areas of the film to pucker in a manner indicating that the affected region was no longer "strictly amorphous". Our present technique utilizes a single copper plug with a central region $5/8$ " diameter which was machined to $.001$ " thick. The copper plug was screwed into a cooled copper block through which liquid nitrogen was circulated. The single block substrate holder maintained the film cold and amorphous while it was being formed, provided that the evaporation rate and thermal radiation from outside sources were carefully controlled. A film which undergoes an amorphous to crystalline transition also undergoes a change in its dimensions. The forces present when the transition occurs are sufficient to disrupt the bond between the substrate and the film. Thin amorphous films ($\sim 1\mu$) seem to adhere to the substrate fairly well when cycled up to room temperature; films thicker than $\sim 2\mu$ invariably crumble and peel off the substrate. A boron nitride cap to protect the film during the warming up process has been employed to prevent the film from flaking away.

Films deposited on room temperature substrates are crystalline, easily prepared, and may be made quite thick - up to 10 microns or more. These films are of good appearance, smooth, and adhere to the substrate despite repeated cycling between room and liquid nitrogen temperatures. The Mossbauer spectra are very similar to those obtained using pure tellurium metal powder ground up with a binder (typically household sugar) and encapsulated in a nylon wafer holder. Both types of samples,

crystalline films and powder, exhibited a marked intensity asymmetry in the components of the quadrupole doublet. We have traced the origin of the asymmetry to a preferred orientation direction in both kinds of samples. This is not surprising for the films, which clearly have a preferential direction of growth. The powder samples show a preferred packing orientation, an unexpected phenomenon, which has nevertheless been observed in other systems ⁽⁸⁾ when the matrix material is soft compared with the Mossbauer active crystalline component. Grinding the tellurium powder thoroughly with fine powdered alumina as a matrix material produces a spectrum with a very small residual asymmetry. This result demonstrates that the asymmetry is largely an orientation or sample preparation problem. It is doubtful that there is any intrinsic asymmetry in the polycrystalline tellurium metal spectrum ⁽⁹⁾.

d) Mossbauer Experiments

Several spectra of crystalline tellurium films have been obtained for a number of different samples. The analysis, which will not be presented in detail at this time, shows that all the crystalline films are oriented with respect to the deposition surface, as mentioned earlier, and that the quadrupole splitting, isomer shift, and recoil free fraction are all essentially the same as for polycrystalline tellurium powder ⁽¹⁰⁾.

Amorphous tellurium films have been prepared and the Mossbauer spectra obtained. The same films were then crystallized by warming to room temperature and then re-run on the Mossbauer spectrometer. In both cases (amorphous and crystalline), the source and absorber were at liquid nitrogen temperature while the Mossbauer spectra were being accumulated. Notwithstanding our dissatisfaction with the quality of the amorphous films, it is clear from Figure 1, as well as from several other spectra of different samples, that the amorphous and crystallized samples produce remarkably different spectra. Most obvious is the large difference in the overall intensities. The total integrated area under the crystallized sample is at least three times the area of the same sample before it was crystallized. In addition, the quadrupole splitting, assuming it is unique in each case, is $\sim 20\%$ larger in the amorphous phase than in the crystalline phase. The dominant effect is the observation of a reduced recoil free fraction in the amorphous phase which we interpret as being due to the weaker binding between tellurium atoms in the amorphous phase. Raman scattering experiments on amorphous and crystalline tellurium films ⁽¹¹⁾ seem to corroborate this hypothesis based on an analysis of the phonon spectra for the two phases. Although not directly presenting a phonon density of states, the Raman results ⁽¹¹⁾ indicate in a qualitative way that the phonon spectrum for the amorphous phase is considerably softer

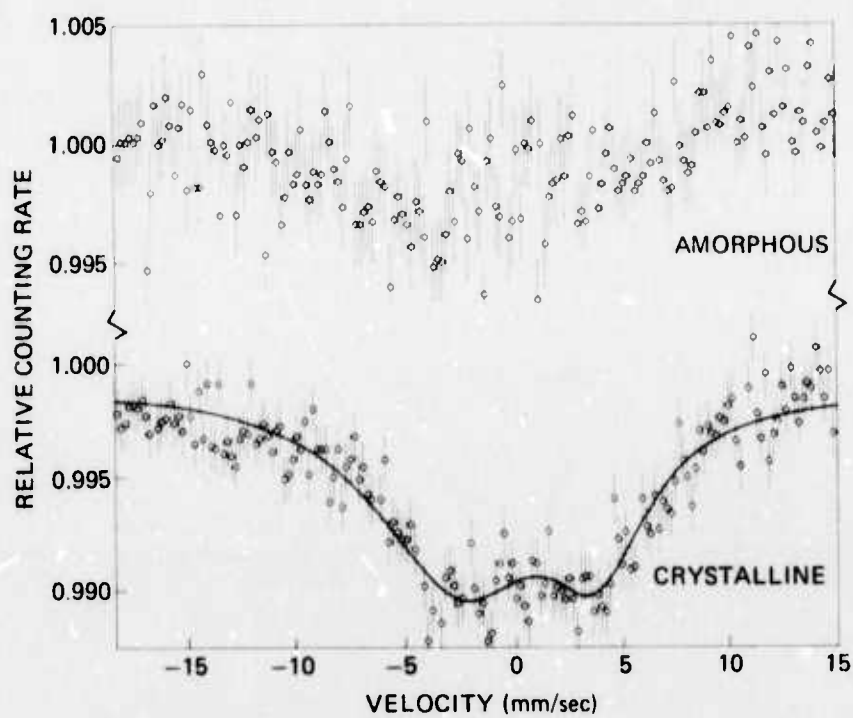


FIGURE 1 MOSSBAUER ABSORPTION SPECTRA OF 1μ THICK
TELLURIUM FILM (ENRICHED 50% Te-125)

(i.e., higher density of low energy components) than the corresponding spectrum for the polycrystalline phase. The increased quadrupole splitting in the amorphous samples may be interpreted in terms of a corresponding change in the tellurium covalent bond lengths. If additional and hopefully better resolved, spectra indicate that the quadrupole splitting is unique (or nearly so), it may be possible to correlate the softer phonon modes with the quantitatively determined change in the bond lengths to provide a reasonable microscopic picture of amorphous tellurium.

In the experiments performed so far, the thicker amorphous films gave a sufficiently well resolved spectrum to measure the quadrupole splitting. Unfortunately these thicker films turned to powder and flaked off the substrate when the samples were warmed to room temperature. This, of course, destroyed the possibility of making a measurement on the crystallized sample. In Figure 1 we see spectra for a sample which was thick enough to give a good crystallized spectrum and thin enough to remain adhering to the substrate. The amorphous spectrum, however, reflects the low recoil free fraction, but is too thin to give a spectrum in which the parameters may be measured with any accuracy.

C. FUTURE PLANS

The vacuum deposition apparatus is being slightly altered in order to improve the cooling of the samples during deposition. The deposition of amorphous films of the requisite thickness (~ 4 microns) is a delicate procedure which requires considerable experience and patience. The dramatic difference between the amorphous and polycrystalline sample spectra shown in Figure 1 shows that we have succeeded in carrying out the principal objective of this program, namely: to show that the Mossbauer technique is useful for studying order-disorder transformations in solids. In order to obtain consistent and better resolved spectra than those shown in Figure 1 we shall need thicker uniform films possibly enriched up to 95% in ^{125}Te .

A further improvement in spectral resolution may be expected to result from our efforts to obtain a better Mossbauer source. The line width in ^{125}Te Mossbauer spectroscopy is marginal for detailed quantitative studies of multi-line quadrupole interactions and isomer shifts. Any improvement in recoil free fraction and narrowing of the emission line would help in the detailed data analysis. The development of such a source would greatly benefit all workers in the field of tellurium Mossbauer spectroscopy. We are thus continuing to investigate improved Mossbauer sources for the tellurium-125 spectroscopy. In particular, in collaboration with the New England Nuclear Corporation, we are evaluating a new method of preparing

β -TeO₃ sources and the feasibility of using sources incorporating 2.7 year ¹²⁵Sb.

The data will be analyzed quantitatively and correlated with information on the amorphous/crystalline tellurium system obtained by other experimental techniques as well as with contemporary theoretical models.

The temperature of the amorphous to crystalline transition and the nature of the crystallization process (2) will be investigated using a resistivity bridge technique. Eventually we hope to be able to correlate these results with optical transmission measurements (13).

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